FORM PTO 1390 (REV 5-93) US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371

ATTORNEY DOCKET NUMBER 2001_0094A

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) NEW 09/762100

International Application No.	**International Filing Date**	**Priority Date Claimed**
PCT/JP99/04199	August 4, 1999	August 4, 1998

Title of Invention
NONLINEAR OPTICAL CRYSTAL

Applicant(s) For DO/EO/US: Takatomo SASAKI; Yusuke MORI and Masashi YOSHIMURA

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.

2. [] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.

3. [X] This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).

4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. [X] A copy of the International Application as filed (35 U.S.C. §371(c)(2))
   a. [] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [X] has been transmitted by the International Bureau.
   c. [] is not required, as the application was filed in the United States Receiving Office (RO/US)

6. [X] A translation of the International Application into English (35 U.S.C. §371(c)(2)).

7. [X] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)).
   a. [] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [] have been transmitted by the International Bureau.
   c. [] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [X] have not been made and will not be made.

8. [] A translation of the amendments to the claims under PCT Article 19.

9. [X] An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)). (Unexecuted)

10. [] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

Items 11. to 14. below concern other document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. [] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. [X] A FIRST preliminary amendment.

    [] A SECOND or SUBSEQUENT preliminary amendment.

14. [X] Other items or information: (a) Form PCT/IB/308; (b) International Search Report; and (c) First page of published international application (WO 00/08524).

U.S. APPLICATION NO. (If known, see 37 CFR 1.5) NEW 09/762100	INTERNATIONAL APPLICATION NO. PCT/JP99/04199	ATTORNEY'S DOCKET NO. 2001_0094A

15. [X] The following fees are submitted	CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):		
Neither international preliminary examination fee nor international search fee paid to USPTO and International Search Report not prepared by the EPO or JPO $1000.00		
International Search Report has been prepared by the EPO or JPO ..... $ 860.00		
International preliminary examination fee not paid ot USPTO but international search paid to USPTO ..... $ 710.00		
International preliminary examination fee paid to USPTO but claims did not satisfy provisions of PCT Article 33(1)-(4) ..... $ 690.00		
International preliminary examination fee paid ot USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... $ 100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$860.00	
Surcharge of $130.00 for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

Claims	Number Filed	Number Extra	Rate		
Total Claims	12 -20 =	0	X $18.00	$	
Independent Claims	1 - 3 =	0	X $80.00	$	
Multiple dependent claim(s) (if applicable)			+ $270.00	$	
TOTAL OF ABOVE CALCULATIONS =				$860.00	
[] Small Entity Status is hereby asserted. Above fees are reduced by 1/2.				$	
SUBTOTAL =				$860.00	
Processing fee of $130.00 for furnishing the English translation later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40 per property +				$	
TOTAL FEES ENCLOSED =				$860.00	
				Amount to be refunded	$
				Amount to be charged	$

a. [X] A check in the amount of $860.00 to cover the above fees is enclosed. A duplicate copy of this form is enclosed.

b. [] Please charge my Deposit Account No. 23-0975 in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0975.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

19. CORRESPONDENCE ADDRESS

000513

PATENT TRADEMARK OFFICE

By: Michael R. Davis

Michael R. Davis , Registration No. 25,134

WENDEROTH, LIND & PONACK, L.L.P.
2033 "K" Street, N.W., Suite 800
Washington, D.C. 20006
Phone:(202) 721-8200
Fax:(202) 721-8250

February 2, 2001

THE COMMISSIONER IS AUTHORIZED TO CHARGE ANY DEFICIENCY IN THE FEES FOR THIS PAPER TO DEPOSIT ACCOUNT NO. 23-0975

[CHECK NO. 41832]

[2001_0094A]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	:	
Takatomo SASAKI et al.	:	**Attn: BOX PCT**
Serial No. NEW	:	**Docket No. 2001_0094A**
Filed February 2, 2001	:	
NONLINEAR OPTICAL CRYSTAL **[Corresponding to PCT/JP99/04199** **Filed August 4, 1999]**	:	

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Please amend the above-identified application as follows:

IN THE SPECIFICATION:

Page 1, after the title of the invention, please insert

--This application is a 371 application of PCT/JP99/04199 filed August 4, 1999.--

IN THE CLAIMS:

Please amend the following claims as indicated:

4(amended). A wavelength conversion method of performing wavelength conversion by use of a nonlinear optical crystal according to claim 1.

5(amended). A wavelength conversion element having a construction made of a nonlinear optical crystal according to claim 1.

Please add the following new claims:

--7. A wavelength conversion method of performing wavelength conversion by use of a nonlinear optical crystal according to claim 2.

8. A wavelength conversion method of performing wavelength conversion by use of a nonlinear optical crystal according to claim 3.

9. A wavelength conversion element having a construction made of a nonlinear optical crystal according to claim 2.

10. A wavelength conversion element having a construction made of a nonlinear optical crystal according to claim 3.

11. A wavelength conversion apparatus having a construction in which a wavelength conversion element according to claim 9 is incorporated.

12. A wavelength conversion apparatus having a construction in which a wavelength conversion element according to claim 10 is incorporated.--

REMARKS

The Specification has been amended to insert a cross-reference to the international application on which the present U.S. application is based.

Claims 4 and 5 have been amended to depend only from claim 1, thus avoiding their multiple dependency, as a result of which new claims 7-12 have been added to the application.

Attached hereto is a marked-up version of the changes made to the claims by the current Preliminary Amendment. The attached page is captioned "**Version with markings to show changes made.**"

Respectfully submitted,

Takatomo SASAKI et al.

By _____
Michael R. Davis
Registration No. 25,134
Attorney for Applicants

MRD/sls
Washington, D.C.
Telephone (202) 721-8200
Facsimile (202) 721-8250
February 2, 2001

THE COMMISSIONER IS AUTHORIZED TO CHARGE ANY DEFICIENCY IN THE FEES FOR THIS PAPER TO DEPOSIT ACCOUNT NO. 23-0975

VERSION WITH MARKINGS TO SHOW CHANGES MADE

4. A wavelength conversion method of performing wavelength conversion by use of a nonlinear optical crystal according to ~~any of~~ claims 1 ~~to 3~~.

5. A wavelength conversion method of performing wavelength conversion by use of a nonlinear optical crystal according to ~~any of~~ claims 1 ~~to 3~~.

NONLINEAR OPTICAL CRYSTAL

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to a nonlinear optical crystal. More specifically, the invention relates to a novel nonlinear optical crystal useful as a wavelength conversion crystal for generating vacuum ultraviolet light or the like, and a wavelength conversion method using the wavelength conversion crystal, as well as an element and a wavelength conversion apparatus for use in the method.

BACKGROUND ART

With the development of laser technology, it has become an importance subject to realize solid-state lasers having performance which allows for the applications of laser technology. One such subject is to put into practice all solid-state vacuum ultraviolet laser light sources of shorter wavelength.

To realize an all solid-state vacuum ultraviolet laser light source of short wavelength, there is a need for a nonlinear optical crystal which has a double refraction index of about 0.07 and an absorption edge which lies in the range of short wavelengths of 150-160 nm. As prior art nonlinear optical crystals which satisfy these characteristics, the following

ones have been known:

$Sr_2Be_2B_2O_7$ (SBBO),

$KBe_2BO_3F_2$ (KBBF).

These publicly known prior art SBBO and KBBF, however, have the large problem that both crystals are difficult to obtain, because they are extremely difficult to grow.

SUMMARY OF THE INVENTION

Therefore, the invention provides a nonlinear optical crystal. More specifically, the invention provides a novel nonlinear optical crystal for all solid-state generation of vacuum ultraviolet light, which has the required characteristics and is easy to obtain through crystal growth instead of the prior art SBBO and KBBF, and a wavelength conversion method using such novel nonlinear optical crystal, as well as an element and a wavelength conversion apparatus for use in the method.

To solve the above-described subject, the invention provides a nonlinear optical crystal represented by $K_2Al_2B_2O_7$, and a wavelength conversion method using this nonlinear optical crystal, as well as an element and a wavelength conversion apparatus for use in the method.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will become more readily appreciated and understood from the following detailed description of a preferred embodiment of the invention when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a cross-sectional view of the construction of a growing furnace used in the embodiment;

Fig. 2 is a view showing a result of X-ray diffraction of the structure of a KAB crystal according to the invention; and

Fig. 3 is a view showing another result of X-ray diffraction similar to that shown in Fig. 2.

DETAILED DESCRIPTION OF THE INVENTION

An embodiment of the invention will be described below with reference to a nonlinear optical crystal represented by $K_2Al_2B_2O_7$ (referred to simply as the KAB crystal) which is provided according to the invention. The KAB crystal has a structure in which K and Al are substituted for the respective Sr and Be sites of the publicly known SBBO crystal, i.e., $Sr_2Be_2B_2O_7$, although there is a difference in electric charge between both crystals.

The KAB crystal of this invention has a double refraction index of about 0.07 which is a nature approximately equal to that of the publicly known SBBO crystal. Accordingly, the KAB

crystal is expected to generate vacuum ultraviolet light. The KAB crystal can easily be grown by a method such as a flux method.

The flux method is one kind of solution growth method, and is characterized by TSSG (Top Seeded Solution Growth), i.e., the process in which a seed crystal attached to a rotating shaft is immersed immediately below the surface of a solution to increase the degree of supersaturation by means of a decrease in temperature, thereby growing a crystal. In addition, the flux method is characterized by melting a flux and a source material.

Since the melting point of the KAB crystal is high, it is more preferable to grow the KAB crystal by the flux method (solution growth method) than by a melt method (melt growth method).

In this flux method, the crystal growth can be made far easier by using a flux such as lead oxide, sodium fluoride (NaF), cesium fluoride (CsF), lead fluoride or potassium chloride.

Accordingly, the KAB crystal of the invention is easy to grow and is superior in practical terms, and is extremely useful as a practical nonlinear optical crystal for generating vacuum ultraviolet light.

This crystal is actually utilized as an element for wavelength conversion or a wavelength conversion apparatus incorporated in this element.

Incidentally, it goes without saying that inevitable

trace elements are allowed to be inevitably incorporated into the composition of the crystal of the invention by a growth process or a source material.

This invention will be described below in further detail with reference to an example.

EXAMPLE

Source materials having the following compositions were used to grow a crystal in the growing furnace shown in Fig. 1 by way of example:

K_2CO_3 (34 mol%),

Al_2O_3 (19 mol%),

B_2O_3 (45 mol%),

KCl (2 mol%).

The growing furnace shown in Fig. 1 has a construction like a cylindrical resistance heating furnace. In this furnace, its heater is vertically divided into five layers each of which can be independently controlled. A temperature program setting device capable of controlling temperature in units of a minimum of 0.1°C is used as a control part for the heater, and a quartz tube is disposed between the heater and a crucible so that a steep temperature gradient near the crucible is restrained. The crucible is made of platinum, and is arranged to move up and down by an elevating device lying at the bottom of the furnace, so that the crucible can be charged with a source material in a heated state. In addition, in order to correct

a change in the temperature of the solution surface, a solution surface heater is disposed to prevent a decrease in temperature due to evaporation near the solution surface, thereby providing a temperature distribution optimum for crystal growth. At a temperature of about 1,000°C, the source material was melted in the atmospheric air, and was then cooled to grow into a microcrystal. The rate of temperature decrease was 0.2-0.3 °C/day, and the speed of rotation was 30 rpm (the direction of rotation was reversed at intervals of 3 minutes).

Through the above-described growth, a crystal of size about 3 mm was obtained.

The result of an analysis using plasma emission spectrometry (ICP) showed that this crystal had the composition of $K_2Al_2B_2O_7$. As is apparent from the result of four circle X-ray diffractometry shown in Figs. 2 and 3, it was confirmed that the structure of the obtained crystal was similar to that of the SBBO crystal but K and Al were 100% substituted for its Sr and Be sites, respectively.

In the evaluation of wavelength conversion characteristic (nonlinearity) of the crystal, when the crystal was illuminated with the fundamental light (wavelength 1,064 nm) of a Nd:YAG laser, the occurrence of light of second harmonic (532 nm) was confirmed.

In addition, when the double refraction index of this crystal was measured by an oil immersion method, it was

confirmed that the value was 0.07 and was approximately equal to that of the SBBO crystal.

It is to be noted that since the shortest SHG wavelength of the prior art KBBF crystal is 185 nm or less and that of the prior art SBBO crystal is 200 nm or less, the KAB crystal of this invention can be phase-matched to approximately 200 nm. The absorption edge of the KAB crystal was 180 nm or less.

In addition, the growth of the KAB crystal of this invention is far easy and far efficient compared to the case of SBBO and KBBF.

Incidentally, the Vickers hardness of the grown KAB crystal was about 300, and from the result of a water resistance test using immersion at room temperature, it was confirmed that the KAB crystal did not melt even after the passage of ten days or more.

In accordance with the invention, there is provided a $K_2Al_2B_2O_7$ (KAB) crystal as a vacuum ultraviolet light generating nonlinear optical crystal which is easy to grow and of high practical use, and a wavelength conversion method using this crystal, as well as an element and a wavelength conversion apparatus for use in the method.

What is Claimed is:

1. A nonlinear optical crystal represented by the formula: $K_2Al_2B_2O_7$.

2. A nonlinear optical crystal according to claim 1, which is solution growth by use of a flux.

3. A nonlinear optical crystal according to claim 2, where the flux is at least one kind selected from among lead oxide, sodium fluoride, cesium fluoride, lead fluoride or potassium chloride.

4. A wavelength conversion method of performing wavelength conversion by use of a nonlinear optical crystal according to any of claims 1 to 3.

5. A wavelength conversion element having a construction made of a nonlinear optical crystal according to any of claims 1 to 3.

6. A wavelength conversion apparatus having a construction in which a wavelength conversion element according to claim 5 is incorporated.

ABSTRACT

There is provided a nonlinear optical crystal which is presented by the formula: $K_2Al_2B_2O_7$. This nonlinear optical crystal is a vacuum ultraviolet light generating nonlinear optical crystal which is easy to grow and of high practical use. There are also provided a wavelength conversion method using this crystal, and an element and a wavelength conversion apparatus for use in the method.

Fig. 1

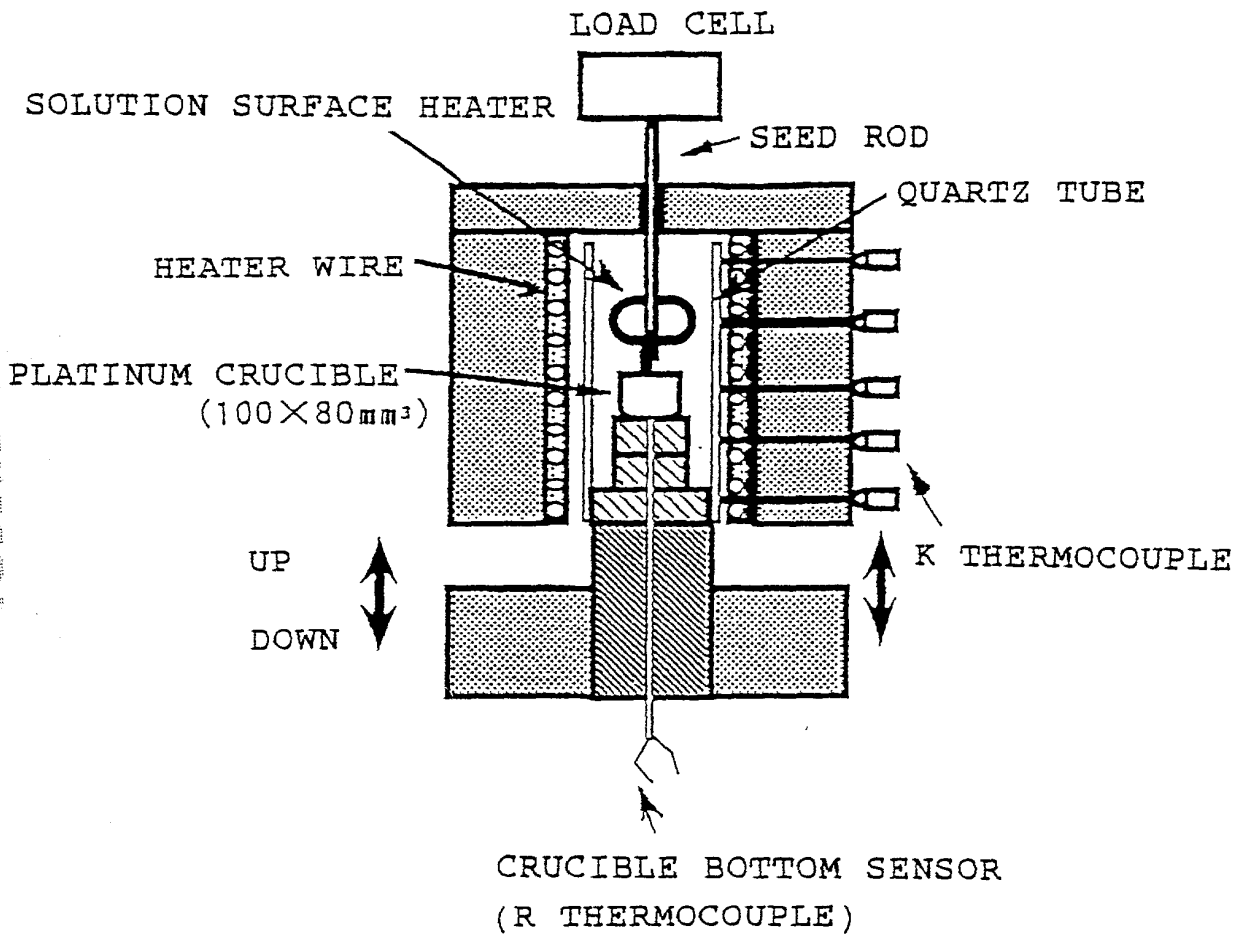

LOAD CELL
SOLUTION SURFACE HEATER
SEED ROD
QUARTZ TUBE
HEATER WIRE
PLATINUM CRUCIBLE
(100×80mm³)
UP
DOWN
K THERMOCOUPLE
CRUCIBLE BOTTOM SENSOR
(R THERMOCOUPLE)

Fig. 2

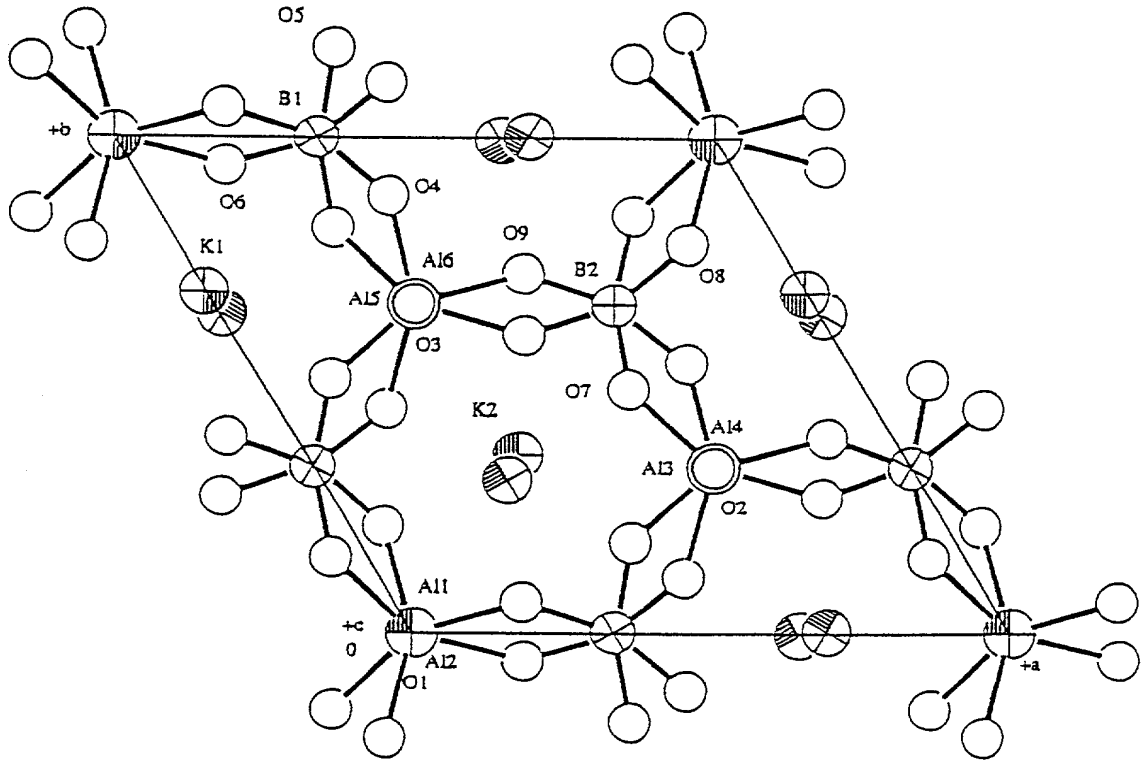
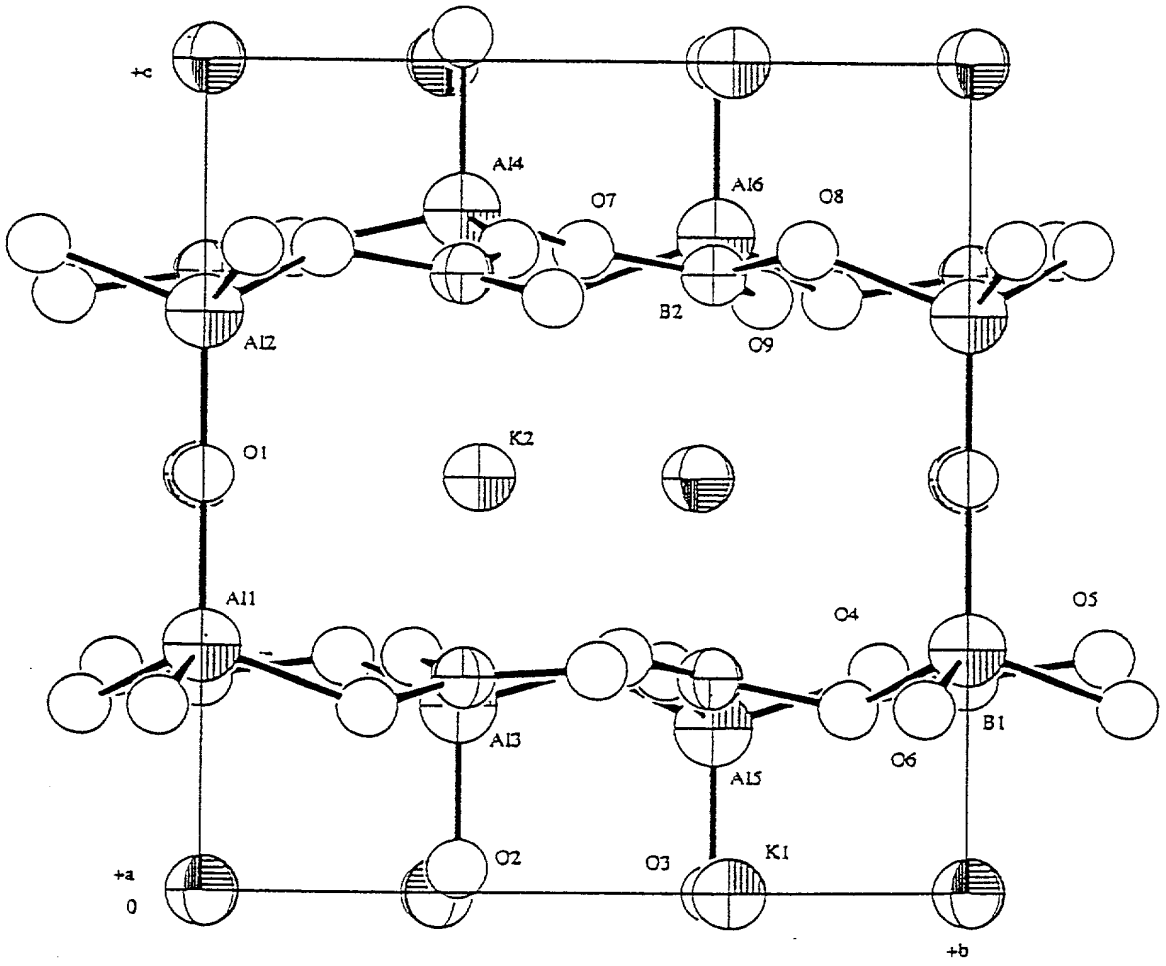


Fig. 3



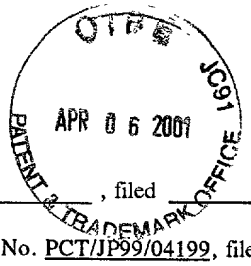
Rev. 1-16-01

Effective March 1998

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION

(X) Original () Supplemental () Substitute () PCT () DESIGN

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:



Title: NONLINEAR OPTICAL CRYSTAL

of which is described and claimed in:
() the attached specification, or
() the specification in application Serial No. _____, filed _____, and with amendments through _____,
or
(X) the specification in International Application No. PCT/JP99/04199, filed August 4, 1999, and as amended on (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any application(s) for patent or inventor's certificate listed below and have also identified below any application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
Japan	220914/1998	August 4, 1998	YES

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

And I hereby appoint Michael R. Davis, Reg. No. 25,134; Matthew M. Jacob, Reg. No. 25,154; Warren M. Cheek, Jr., Reg. No. 33,367; Nils Pedersen, Reg. No. 33,145; Charles R. Watts, Reg. No. 33,142; and Michael S. Huppert, Reg. No. 40,268, who together constitute the firm of WENDEROTH, LIND & PONACK, L.L.P., as well as any other attorneys and agents associated with Customer No. 000513, to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys and agents named herein to accept and follow instructions from NISHIZAWA & ASSOCIATES as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

Direct Correspondence to Customer No:	Direct Telephone Calls to:
000513	WENDEROTH, LIND & PONACK, L L P. 2033 "K" Street, N W., Suite 800 Washington, D C 20006 Phone (202) 721-8200 Fax (202) 721-8250

Full Name of First Inventor	FAMILY NAME SASAKI	FIRST GIVEN NAME Takatomo	SECOND GIVEN NAME	
Residence & Citizenship	CITY Suita-shi	STATE OR COUNTRY Japan	COUNTRY OF CITIZENSHIP Japan	
Post Office Address	ADDRESS A-9-310, 2-8 Yamadanishi, Suita-shi, Osaka, Japan	CITY	STATE OR COUNTRY	ZIP CODE
Full Name of Second Inventor	FAMILY NAME MORI	FIRST GIVEN NAME Yusuke	SECOND GIVEN NAME	
Residence & Citizenship	CITY Osaka	STATE OR COUNTRY Japan	COUNTRY OF CITIZENSHIP Japan	
Post Office Address	ADDRESS 8-16-9, Kisaichi, Katano-shi, Osaka, Japan	CITY	STATE OR COUNTRY	ZIP CODE
Full Name of Third Inventor	FAMILY NAME YOSHIMURA	FIRST GIVEN NAME Masashi	SECOND GIVEN NAME	
Residence & Citizenship	CITY Hiroshima	STATE OR COUNTRY Japan	COUNTRY OF CITIZENSHIP Japan	
Post Office Address	ADDRESS 2-10, Nobuhiro-cho, Fukuyama-shi, Hiroshima, Japan	CITY	STATE OR COUNTRY	ZIP CODE
Full Name of Fourth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP	
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY	ZIP CODE
Full Name of Fifth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP	
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY	ZIP CODE

I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor Takatomo Sasaki Takatomo SASAKI Date April 4, 2001

2nd Inventor Yusuke Mori Yusuke MORI Date April 4, 2001

3rd Inventor Masashi Yoshimura Masashi YOSHIMURA Date April 4, 2001

4th Inventor _____ Date _____

5th Inventor _____ Date _____

6th Inventor _____ Date _____

The above application may be more particularly identified as follows:

U.S. Application Serial No. 09/762,100 Filing Date February 2, 2001

Applicant Reference Number 99-F-040PCT-US/NT Atty Docket No. 2001_0094A

Title of Invention NONLINEAR OPTICAL CRYSTAL